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(54) Title: A METHOD OF OXIDISING CARBOHYDRATES

(57) Abstract

In a method of oxidising carbohydrates, particularly starch and dextrin, the oxidation is effected by molecular oxygen in an alkaline aqueous medium in the presence of a catalytic quantity of a metal ion selected from the metals of group VIII of the periodic table, copper or silver and a substance which acts as a ligand for the metal ion and is preferably constituted by a polydentate amine ligand.

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A method of oxidising carbohydrates

The present invention relates to a method of oxidising carbohydrates, particularly starches, dextrin and hydrolysis products thereof.

Oxidised starches are used widely in the paper and textile industries. The product is generally produced by treating starch with hypochlorite in an alkaline aqueous medium. Alternatively, oxidised starches are produced by oxidation with periodate which can cleave the glucoside unit of starch between the C-2 and C-3 atoms which are converted into aldehyde groups. The starch thus produced is used mainly in the production of paper which retains good mechanical strength when wet.

A further potential application of oxidised starch or cellulose, described in German patent application DE-A-24 36 843 is its use as a builder for detergents. The products produced by oxidation with hypochlorite or periodate and subsequently with chlorite contain many carboxylic groups in a chain and thus have good sequestering powers. Their use is limited, however, by the fact that these substances are less biodegradable the higher their degree of oxidation.

The main object of the present invention is to provide an oxidation method which is particularly cheap and advantageous as regards the reagents used in the method. A further object is to provide a method which, with particular reference to the oxidation of starches, gives rise to an oxidation product with improved biodegradability characteristics.

This object is achieved by a method of oxidising carbohydrates, characterised in that the oxidation is effected by means of an oxygen containing gas in an alkaline aqueous medium in the presence of a catalytic quantity of a metal ion selected from the metals of group VIII of the periodic table, copper and silver and a substance which acts as a ligand for the metal ion.

Carbohydrates, which constitute the substrate to which the oxidation method of the invention is applied, include starch, hydrolysis products thereof with up to 1 glucoside unit, and simple carbohydrates such as sorbitol.

The term starch essentially means starch which has not been modified chemically and thus includes carbohydrates of natural and vegetable origin in general which are composed essentially of amylose and/or amylopectin. Native starches extracted from various plants such as potatoes, rice, tapioca, maize and cereals may be used. Of these, maize starch is preferred. Hydrolysis products of starch are constituted by mixtures of oligomers with various numbers of glucoside units, including glucose monomer. These hydrolysis products are easily obtainable, for example, by enzymatic hydrolysis, preferably with the use of endoenzymes. Substrates usable for the invention also include polyols with carbohydrate structure, such as sorbitol.

The metal ion used is preferably iron, copper, silver, cobalt or nickel and is introduced into the alkaline aqueous medium by means of a soluble salt, preferably constituted by a chloride or a sulphate.

Typically, th metal ion is us d in a molar ratio of between 1 and 0.25% with reference to the number of moles of glucoside units in the substrate.

The ligand for the metal ion is preferably a polydentate amine ligand. Of these the following are contemplated:

- monoamines of the general formula:

$$\begin{array}{l} \quad / \; R_1 \\ N \; -R_2 \\ \quad \backslash \; R_3 \end{array}$$

in which one of the radicals R_1, R_2 and R_3 is selected from the group consisting of hydrogen, C_1-C_4 alkyl groups and carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms, and the rest of the R_1, R_2 or R_3 radicals are the same or different carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms, and

- polyamines of the general formula:

$$\begin{array}{ccccc} R_3 & & & & R_1 \\ & \backslash & & / & \\ & N & - R - & N & \\ & / & & \backslash & \\ R_4 & & & & R_2 \end{array}$$

in which R is an alkylene group with from 1 to 4 carbon atoms, preferably ethylene, and

R_1, R_2, R_3, and R_4 are the same or different and are radicals selected independently of each other from the

group consisting of hydrog n, C_1-C_4 alkyl groups, aminoalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms and carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms,

or alternatively, R_1 and R_2 and/or R_3 and R_4 form a heterocyclic ring with the respective nitrogen atom,

or alternatively, R_1, R_2, R_3 and R_4 form heterocyclic groups with the respective nitrogen atoms. Of the preferred amine and polyamine ligands, nitrilotriacetic acid, iminodiacetic acid, ethylenediamine, diethylenetriamine, triethylenetetramine, ethylenediaminetetra-acetic acid (EDTA), ethylenediaminetriacetic acid, phenanthroline and 2,2'-dipyridyl are contemplated in particular.

A combination of EDTA with ferrous sulphate or ferrous chloride is particularly advantageous for the oxidation of starch and hydrolysis products thereof, including glucose.

The oxidation reaction is carried out by bubbling molecular oxygen or air through the alkaline aqueous medium which generally has a pH of from 8 to 14 and typically between 8 and 10 at a temperature of from 25 to 90°C and at atmospheric pressure with vigorous stirring.

Example 1.

40 g of dextrin was dissolved in 500 ml of deionised water. 0.63 g of $FeCl_2$ and 0.5 g of o-phenanthroline were added. The reaction was carried out at 60°C and at a pH of 9 in an atmospher of oxygen and good stirring was maintained. A total of 15 ml of 3.4M

NaOH was introduced during a reaction period of 8 hours. Upon completion of the reaction the wat r was evaporated and the product recovered.

Example 2.

40 g of dextrin was dissolved in 500 ml of deionised water. 0.68 g of $FeSO_4.7H_2O$ and 0.5 g of o-phenanthroline were added. The reaction was carried out at 70°C and at a pH of 9 in an atmosphere of oxygen and good stirring was maintained.

A total of 35 ml of 3.4M NaOH was introduced during a reaction period of 12 hours. Upon completion of the reaction, the water was evaporated and the product recovered.

Example 3.

40 g of dextrin was dissolved in 500 ml of deionised water. 0.34 g of $FeSO_4.7H_2O$ and 25 g of o-phenanthroline were added. The reaction was carried out at 70°C and at a pH of 9 in an atmosphere of oxygen and good stirring was maintained.

A total of 60 ml of 3.4M NaOH was introduced during a reaction period of 32 hours. Upon completion of the reaction the water was evaporated and the product recovered.

Example 4.

40 g of dextrin was dissolved in 500 ml of deionised water. 0.34 g of $FeSO_4.7H_2O$ and 0.43 g of the dihydrated disodium salt of EDTA were added. The

reaction was carried out at 70°C and at a pH of 9 in an atmosphere of oxygen and good stirring was maintained.

A total of 60 ml of 3.4M NaOH was introduced during a reaction period of 16 hours. Upon completion of the reaction the water was evaporated and the product recovered.

Example 5.

20 g of soluble starch was dissolved in 500 ml of deionised water. 0.34 g of $FeSO_4.7H_2O$ and 0.25 g of o-phenanthroline were added. The reaction was carried out at 70°C and at a pH of 9 in an atmosphere of oxygen and good stirring was maintained.

A total of 17 ml of 3.4M NaOH was introduced during a reaction period of 12 hours. Upon completion of the reaction the water was evaporated and the product recovered.

Example 6.

20 g of maize starch was gelled in 500 ml of deionised water. 0.34 g of $FeSO_4.7H_2O$ and 0.46 g of EDTA were added in an atmosphere of oxygen and good stirring was maintained.

A total of 17 ml of 3.4M NaOH was introduced during a reaction period of 17 hours. Upon completion of the reaction the water was evaporated and the product recovered.

The recovered product was subjected to Ft-IR spectroscopy with Perkin Elmer 1760 equipment. The

graph below shows the spectra of the oxidation product (2) and of untreated starch (1) in Nujol.

The spectrum (2) has a band at a wavelength of 1597 cm^{-1} which is characteristic of the salified carboxyl group and is absent from the spectrum (1). The two spectra have substantially corresponding shapes in the region between 1000 and 1100 cm^{-1} in which there are strong bands characteristic of the structure of starch.

The oxidation product of a starch or a dextrin obtainable by the method which is described above and is the subject of the following claims falls within the scope of the present invention.

The oxidation product of starch may conveniently be used as a binding additive for paper, as a builder for detergents, as a polyelectrolyte thickening agent, in formulations for paints and printing inks, and as a high-molecular-weight coalescent.

Its use as a builder for detergents is particularly advantageous by virtue of its good sequestering properties combined with the biodegradability of the product compared with products oxidised by hypochlorite.

Additionally the product may be used as a co-builder in detergent formulations in association with known builders, such as zeolites, in order to improve the anti-redeposition properties and dispersion capacity of the detergents and achieve an improved soil removal effectiveness.

Hydrolysis products of starch and particularly dextrin oxidised by the method of the invention may also be used in particular as polyelectrolyte thickening agents in formulations for paints and printing inks. These uses constitute a further subject of the invention.

CLAIMS

1. A method of oxidising carbohydrates, characterised in that the oxidation is effected by means of an oxygen containing gas in an alkaline aqueous medium in the presence of a catalytic quantity of a metal ion selected from the metals of group VIII of the periodic table, copper and silver and a substance which acts as a ligand for the metal ion.

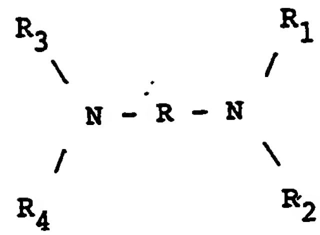
2. A method according to Claim 1, characterised in that the ligand is a polydentate amine ligand.

3. A method according to Claim 2, characterised in that the ligand is a monoamine of the general formula:

$$N \begin{array}{l} / \, R_1 \\ -R_2 \\ \backslash \, R3 \end{array}$$

in which one of the radicals R_1, R_2 and R_3 is selected from the group consisting of hydrogen, C_1-C_4 alkyl groups and carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms and the rest of the R_1, R_2 and R_3 radicals are the same or different carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms.

4. A method according to Claim 2, characterised in that the ligand is a polyamine of the general formula:



in which R is a C_1-C_4 alkylene group, preferably ethylene, and

R_1, R_2, R_3, and R_4 are the same or different and are selected independently of each other from the group consisting of hydrogen, C_1-C_4 alkyl groups, aminoalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms and carboxyalkyl radicals in which the alkyl group has from 1 to 4 carbon atoms,

or alternatively, R_1 and R_2 and/or R_3 and R_4 form a heterocyclic ring with the respective nitrogen atom,

or alternatively, R_1, R_2, R_3 and R_4 form heterocyclic groups with the respective nitrogen atoms.

5. A method according to Claim 2, characterised in that the amine ligand is selected from the group consisting of nitrilotriacetic acid, iminodiacetic acid, ethylenediamine, diethylenetriamine, triethylenetetramine, ethylenediaminetriacetic acid, ethylenediaminetetra-acetic acid, phenanthroline and 2,2'-dipyridyl.

6. A method according to Claim 5 in which the ligand is ethylenediaminetetra-acetic acid and the metal ion is iron.

7. A method according to Claim 5 in which the metal ion is copper and the ligand is o-phenanthroline.

8. A method according to Claim 1 in which the molar concentration of the metal ion in the reaction medium is from 1 to 0.25% with reference to the number of moles of glucoside in the oxidation substrate.

9. A method according to Claim 1 wherein the oxidation reaction is carried out at a temperature of from 25 to 90°C and at atmospheric pressure with vigorous stirring.

10. A method according to Claim 1 wherein the carbohydrate subjected to oxidation is selected from starch, dextrin, hydrolysis products of starch or dextrin, and sorbitol.

11. An oxidation product of starch, a hydrolysis product of starch or dextrin obtainable by a method according to any one of Claims 1 to 9.

12. The use of an oxidation product of starch, a hydrolysis product of starch or dextrin obtainable by a method according to any one of Claims 1 to 9 as a builder or co-builder for detergents.

13. The use of an oxidation product of starch, a hydrolysis product of starch or dextrin obtainable according to any one of Claims 1 to 9 as a binder for paper, as a polyelectrolyte thickening agent or as a coalescent.

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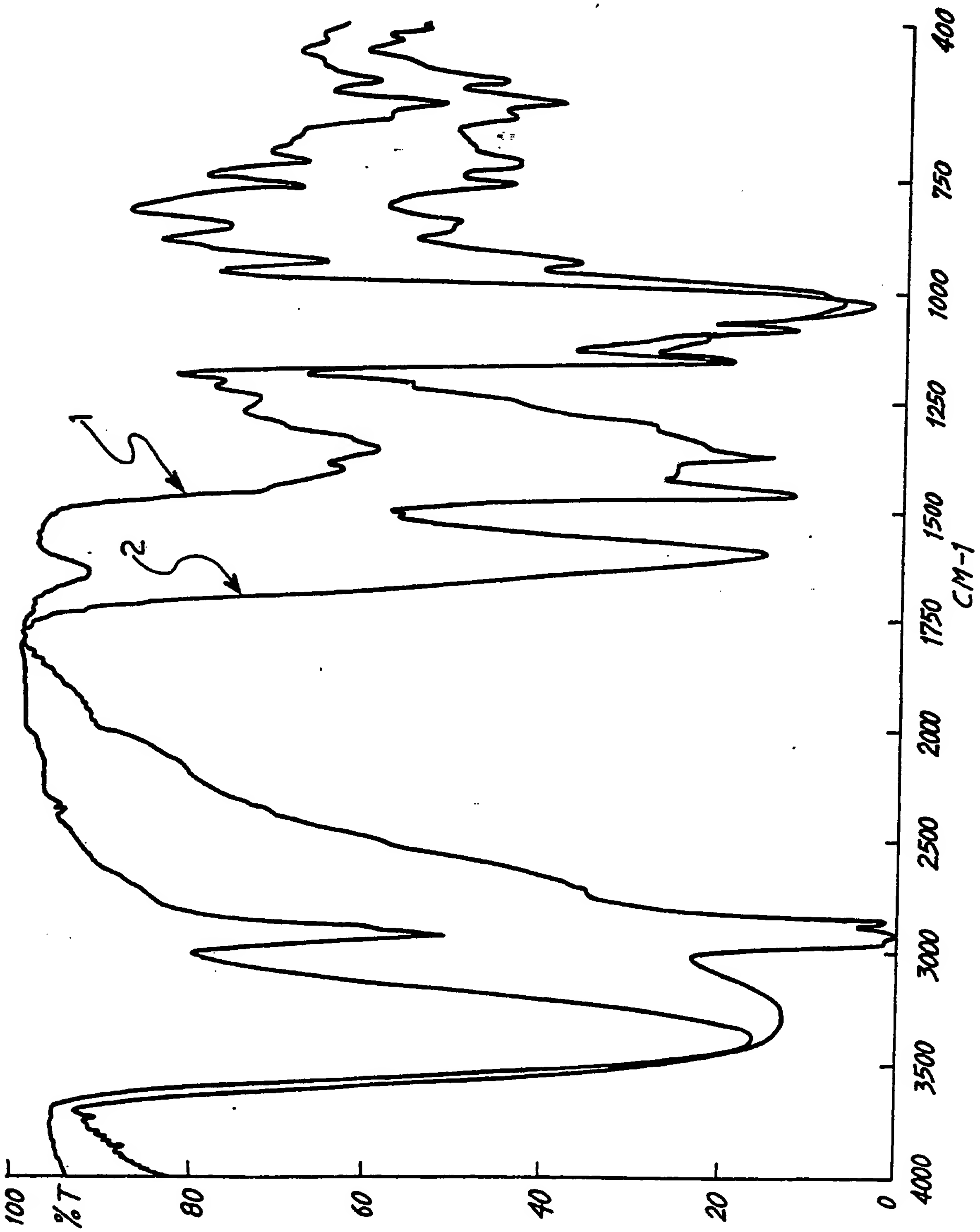
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INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/00827

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08B31/18; C07H7/033; C11D3/22; D21H17/28

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08B ; C07H

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,3 736 224 (M. GRAYSON ET AL.) 29 May 1973 see abstract see column 2, line 24 - line 28 see column 2, line 51 - column 3, line 8 see claims; examples 12,18; table II ---	1,2,9
A	EP,A,0 232 202 (ROQUETTE FRERES) 12 August 1987 see claims ---	1,9,10, 12,13
A	US,A,3 873 614 (LAMBERTI V. ET AL.) 25 March 1975 see abstract see column 8, line 39 - line 47; examples 20,21 ---	1,9,10, 12
A	EP,A,0 378 127 (HOECHST AKTIENGESELLSCHAFT) 18 July 1990 see page 2, line 41 - line 47 see page 3, line 48 - line 50; claims; example 1 --- -/--	1,12

° Special categories of cited documents : [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17 JULY 1992	24. 07. 92
International Searching Authority	**Signature of Authorized Officer**
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 247 314 (HULS AKTIENGESELLSCHAFT) 2 December 1987 see line 40 - line 49 see page 4, line 1 - line 3 ---	1,2,4
A	US,A,4 572 798 (KOTHS ET AL.) 25 February 1986 see column 5, line 38 - line 40 ---	1,2,5,7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9200827 SA 59308

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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